Renewable and Sustainable Energy Reviews 37 (2014) 627–633

Contents lists available at ScienceDirect

Renewable and Sustainable Energy Reviews

journal homepage: www.elsevier.com/locate/rser

A review on structure model and energy system design of lithium-ion battery in renewable energy vehicle

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ARTICLE INFO

Article history:
Received 13 December 2013
Received in revised form
25 March 2014
Accepted 17 May 2014
Available online 7 June 2014

Keywords:
Structure model
Lithium-ion battery
Energy system design
Renewable energy vehicle
Nanostructure
Carbon

ABSTRACT

Structure properties of lithium-ion battery determine the specific energy and specific power of renewable energy vehicle and have attracted extensive concerns. Fundamental innovations in battery system depend on the structure properties, of which graphene and concentration gradient structures become increasingly prospective. As the performance of structure closely relates to the battery performance and the advancement of battery technologies, the paper, based on the research work at our laboratory, discusses about the structure model and energy system design and analyzes the evolution of lithium batteries to provide scientific insights and technical advices for the development of renewable energy vehicle. The review shows that nano and graphene models, with their corresponding energy systems, significantly improve the performance of lithium batteries, thus supporting longer mileage and service life, while providing new ideas for the design of renewable energy vehicles. Compared with other power batteries, lithium-ion batteries are advantageous in addressing the requirements raised by battery electric vehicles, such as, long mileage, high-current charging, and safety. Therefore, lithium batteries are reliable and feasible for the deployment in battery electric vehicles.

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1. Introduction

The whole world's total oil demand is predicted to reach 1500 million tons by year 2030, forming a sharp contradiction between market demand and energy constraints and making transformation in energy utilization imperative [1,2]. Renewable energy vehicle are strategic products to help solve the emission problem. If 30% of all vehicles were transformed to use renewable energy, The whole world would save 22% of its total oil demand [3]. The focus of renewable energy vehicle is on the battery (accounting for approximately half of the total cost) [4], which is required to possess high energy and power densities with fast charging ability at low cost and long lifetime. Energy density enables longer mileage while power density affects the acceleration and climbing performance of vehicles. Structure model and energy system design, therefore, emerges as decisive factors for renewable energy batteries [5]. To assure energy

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http://dx.doi.org/10.1016/j.rser.2014.05.059
1364-0321/

conversion efficiency, battery needs to be charged and discharged frequently, resulting in significant alternations in both voltage and current. But renewable energy vehicle requires battery to maintain power density, charge efficiency, and stability [6].

As traditional batteries cannot provide adequate energy density and power density, more and more vehicles are using lithium batteries because of its high working voltage (3 times of traditional battery) and high energy density (up to 165 Wh/kg, 5 times of traditional battery) [7,8]. Known as "green battery", lithium battery is able to remain stable under extrusion and overcharge, with capacity retention rate exceeding 93% after 1500 cycles, life expectancy of 5–7 years, and monthly self-discharge rate less than 5% [9,10]. The battery consists of electrodes and separator, of which structure functions (micro- and nano-scale characteristics) have significant impact on performance. Based on the technical and economic indicators, lithium ion batteries are primary choice for renewable energy vehicle and play a key role in assuring national energy safety [11]. During the charge–discharge cycles in batteries, lithium ion moves back and forth between anode and cathode, a process similar to a rocking chair, and the system is termed as "rocking-chair battery" [12], as shown in Fig. 1.

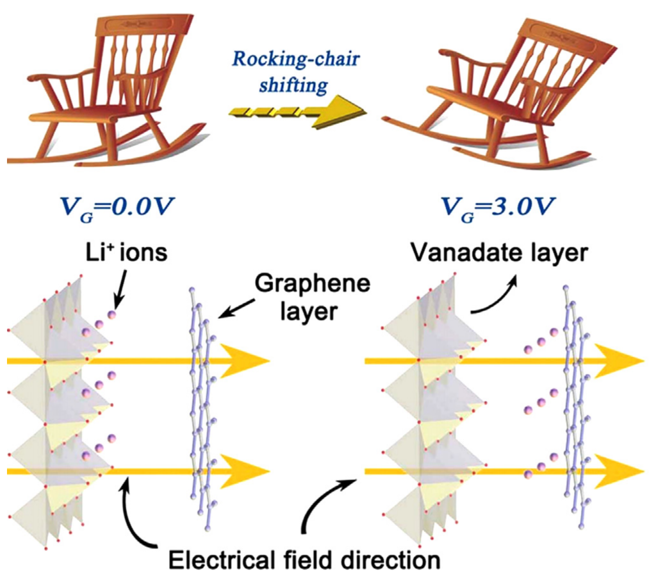

Fig. 1. Rocking-chair graphene battery energy system design and vanadate layer structure model of lithium battery for vehicle [12].

2. Structure model and energy system design for electrode of lithium ion battery

Concentration gradient materials have extensive applications in lithium battery [13,14]. Take Ni/Co binary material for instance, Ni gradually decreases from the interior to the exterior, while Co gradually increases, improving the performance of the composite [15]. At micro-scale level, structure can change the material properties [16], and doping technologies help to enhance conductivity [17]. Such unique structure creates novel properties through material integration and complementation [18]. Hence, research on nanostructure properties becomes a critical sector in recent years [19]. Sun et al. [20] designed a spherical nano-scale gradient structure for Li^+, as shown in Fig. 2, to achieve better magnification and higher tap density. $Li(Ni_{0.8}Co_{0.1}Mn_{0.1})O_2$ is used as inner material for high capacity, while $Li(Ni_{0.46}Co_{0.23}Mn_{0.31})O_2$ at surface for stability under high voltage. The gradient structure allows the material to be made into a thin film of any area in any shape [21]. Lithium ion batteries using such composite film possess a higher capacity. Li et al. [22] created a flexible film structure, as shown in Fig. 3, suitable for high-power charging and discharging, of which the three-dimensional gradient absorbs and retains electrolyte efficiently to assure high conductivity and flexibility. Under large current of discharge the structure generates little heat and the polymerization reactions occurred at high temperatures will close the micropores automatically and resist creep for structural integrity and dimensional stability. Such system becomes a new direction for battery materials.

Guo et al. [23] concluded that $LiFePO_4$ is much safer than traditional materials for applications under large current discharge. The structure of $LiFePO_4$ is orthogonal olivine, as shown in Fig. 4(c), where oxygen atoms stack closely with Fe and Li locating at the center to form octahedrons of FeO_6 and LiO_6. The neighboring FeO_6 octahedrons share one oxygen atom and connect with each other as a layer. Within layers of FeO_6, the neighboring LiO_6 octahedrons are connected via two oxygen atoms so that Li^+ can diffuse in one dimension. The diffusion is one-dimensional along the crystallographic b-axis. Located between layers of FeO_6, PO_4 takes the form of tetrahedron and can block the diffusion of Li^+ to some extent. The structure differs from the continuous structures such as lattice (Fig. 4a) and spinel (Fig. 4b) that have MO_6 octahedron. The multi-wall porous $LiFePO_4$ can be

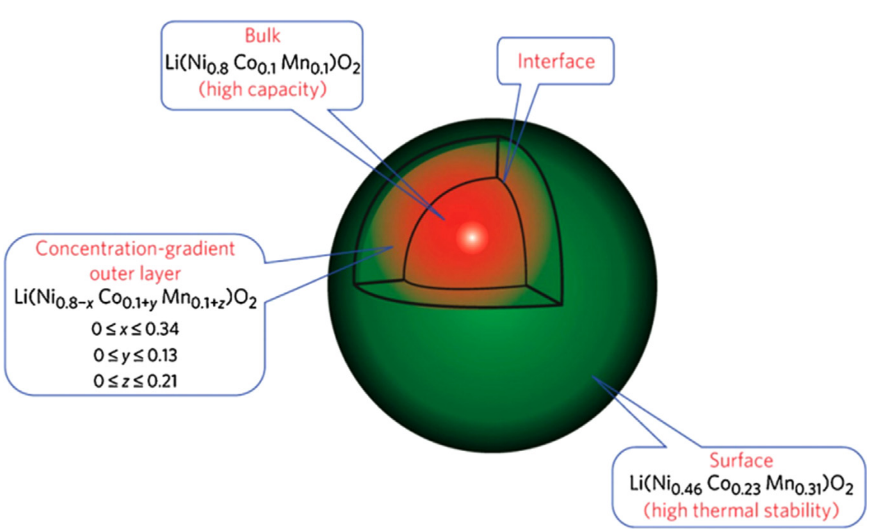

Fig. 2. Spherical gradient structure model and energy system design [20].

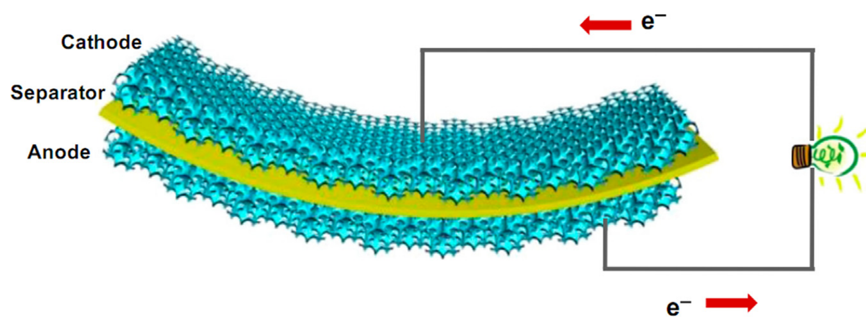

Fig. 3. Flexible film structure model and energy system design [22].

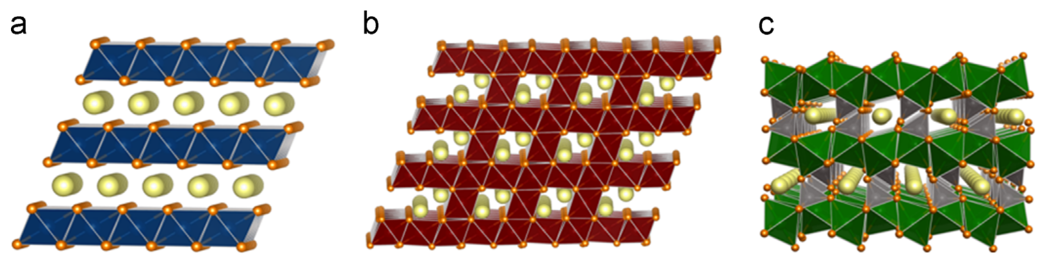

Fig. 4. Comparison of structures of lithium battery energy system [23]: (a) $LiCoO_2$ lattice structure, (b) $LiMn_2O_4$ spinel structure and (c) $LiFePO_4$ olivine structure.

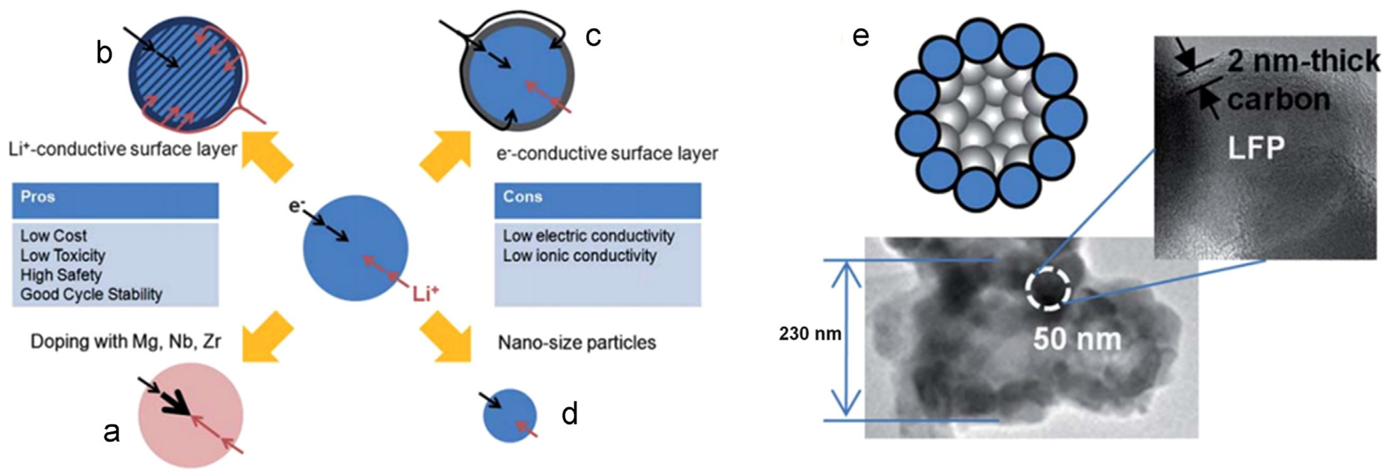

Fig. 5. $LiFePO_4$ nanostructure model and energy system design [24]: (a)–(d) are four nanostructures for higher conductivity and (e) hollow spherical nanostructure with carbon package.

doped with Al^{3+} and Ti^{4+} to obtain conductivity greater than that of $LiCoO_2$ and $LiMn_2O_4$ so as to achieve remarkable discharge capacity with minute polarization and few abnormal particles.

Park et al. [24] analyzed the structure of $LiFePO_4$ and found its electrode potential changes slightly and the voltage is stabilized during the dynamic movement of Li^+ so that the diffusion coefficient can be improved for better cycling performance. Four kinds of structures doped with Mg^{2+} are shown in Fig. 5(a–d). Meanwhile, carbon packaging can further enhance the conductivity of LFP material. The hollow spherical structure, as shown in Fig. 5(e), extends the surface area and tightens the electrolyte for LFP. The structure is able to store energy at 11,000 mAh g^{-1}. The density can be even higher in pure oxygen environment because water in air will affect lithium [25]. To prevent water and facilitate the flowing of oxygen, silicon film can be designed to overcome the disadvantages of traditional batteries.

Chung et al. [26] conducted an in-depth study on structures of $LiFePO_4$, as shown in Fig. 6(a) and (b), and $LiMnPO_4$, as shown in Fig. 6(c) and (d). Compared with $LiMnPO_4$, the structure of $LiFePO_4$ is more suitable for cycles of charge and discharge, in which $LiFePO_4$ coexists with $FePO_4$ after detaching lithium. $FePO_4$ has a similar structure with $LiFePO_4$ and their volume difference is 5.9%, resulting in good cycling performance. Orthogonal experiments show that, as temperature increases to 500 °C, the material's capacity density increases first and then drops during initial discharge. When temperature is too low, the formation of $LiFePO_4$ will be affected. When temperature is too high, the particle size becomes large, thus lowering the diffusion rate of ions. Excessive Fe or Li produces impurity phase. In addition, as lithium volatilizes at high temperature, a short heating period will cause lattice defects but a long heating period will enlarge particle size, obtaining cycle efficiency of 93%. Though graphite coating is able to improve conductivity, it reduces the tap density. Raising the temperature at operation, therefore, helps to increase the diffusion rate of lithium ions. By complementing homogeneous and non-homogeneous nucleation with solid state reaction diffusion under sub-critical and supercritical conditions, the structure of $LiFePO_4$ enables deployment under high temperature [27].

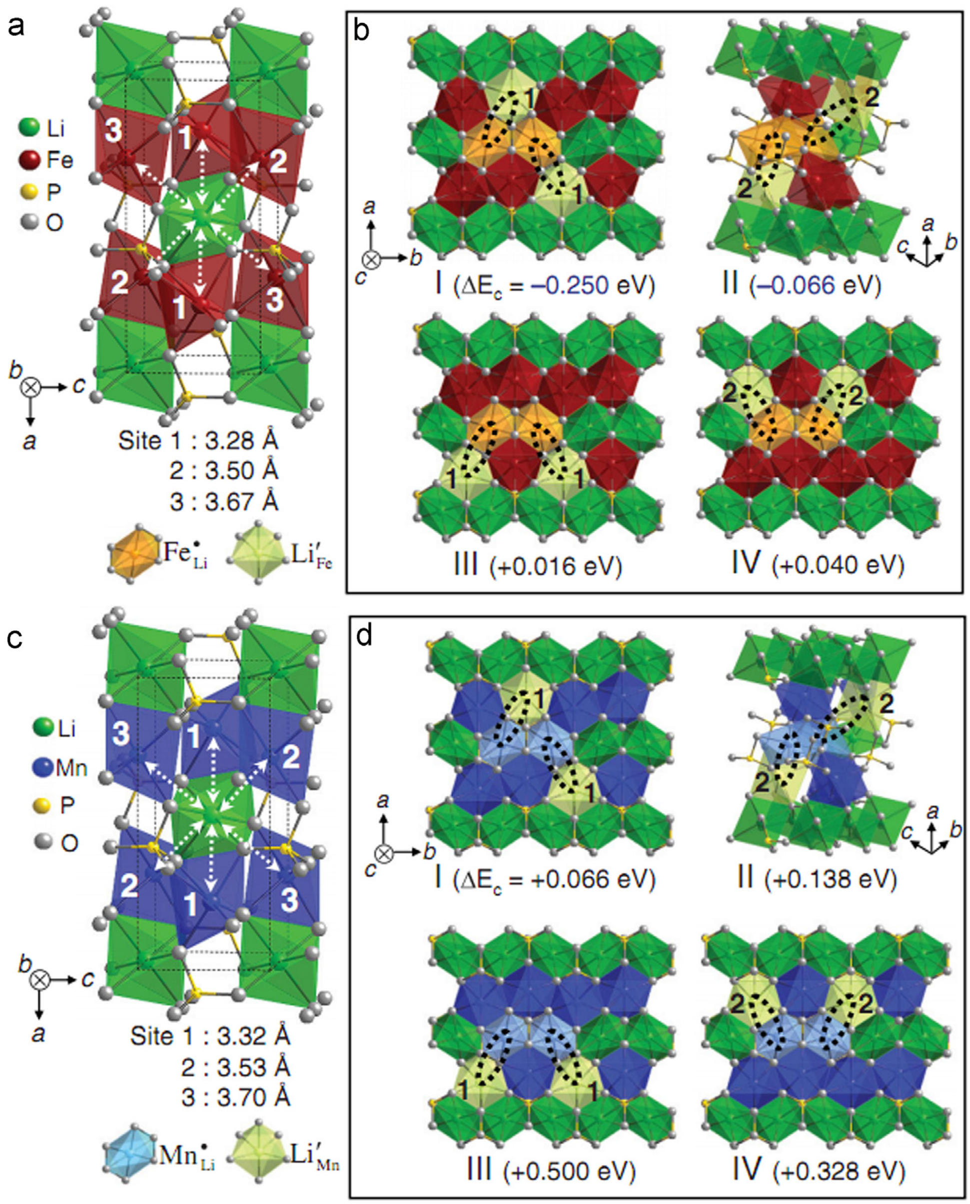

Fig. 6. Structure model of $LiFePO_4$ and $LiMnPO_4$ [26]: (a) single cell structure of $LiFePO_4$, (b) four kinds of link models of $LiFePO_4$, (c) single cell structure of $LiMnPO_4$ and (d) four kinds of link models of $LiMnPO_4$.

3. Structure model and energy system design for graphene lithium ion battery

Energy storage and charging rate are bottlenecks for renewable energy batteries. Battery energy is limited by the capacity of electrodes to hold lithium ions, while charging rate is limited by the speed of lithium ions to pass through electrolyte to reach electrode. Such problem is partly addressed with the advent of graphene. U.S.D.E [28] replaced metallic lithium with reversible graphene material that has a greater surface area per unit mass so that large number of lithium ions can be stored in the electrode to get a much higher energy density than existing batteries, as shown in Fig. 7(a). Connection between graphite atoms is flexible and can effectively prevent electrodes from damage due to volume changes during charge-discharge process and extend the contact area with collectors. When external force is applied, the surface of graphite atoms deforms to adapt to the force without atomic rearranging so that a stable structure is maintained. As published in Science journal, this kind of stable lattice structure has excellent conductivity to improve the material properties of existing lithium ion batteries. Electrons in graphene do not scatter even there are lattice defects.

Due to the strong inter-atomic forces, even the jostling of graphite atoms cannot interfere with the electrons that travel faster than in conductors. Graphene lithium ion battery is a combined structure of high porosity and high distortion based on the nano-scale property. Cao et al. [29] made micro-channels of 10–20 nm on the surface of graphene to broaden pathway for lithium ions which improves the exchange rate and capacity, shortening the charging process by 10 times, as shown in Fig. 7(b). Meanwhile, active substance is embedded in the channels to adhere with current collectors and lower interface resistance for curbing temperature rise [30]. Active electrolyte and graphene form an integral cage to enlarge surface area per unit mass and enhance conductivity. This design is the organic combination between structure and properties of graphene.

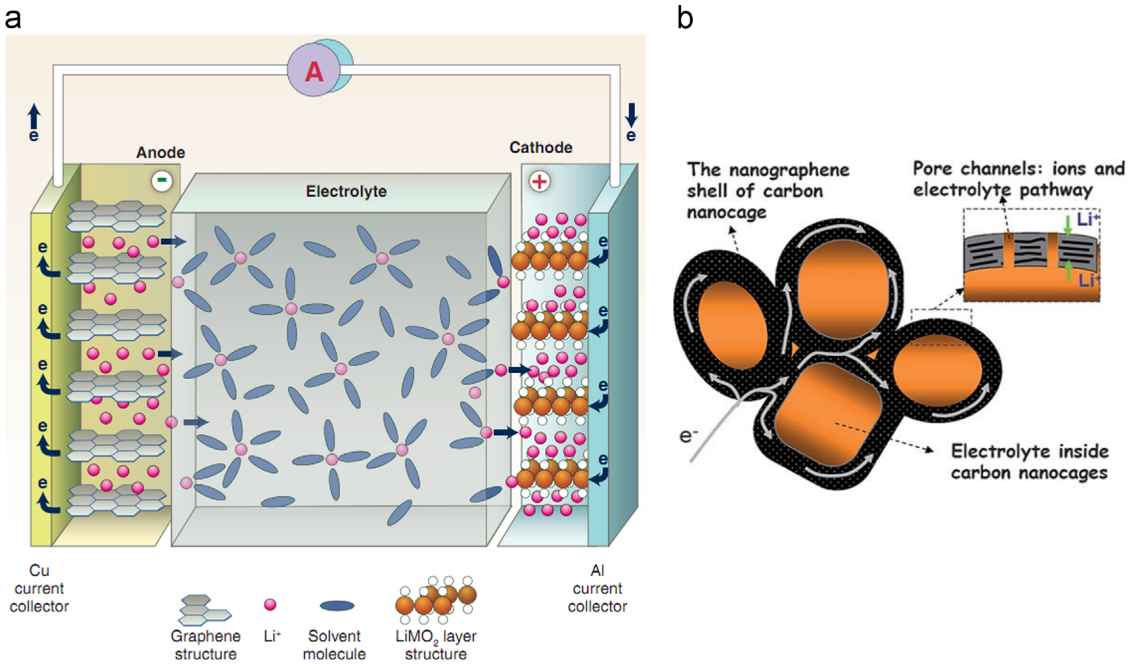

Fig. 7. Structure model and energy system design of graphene lithium ion battery: (a) graphene lithium ion battery structure and energy system design [28] and (b) transport channels in graphene nanostructure [29].

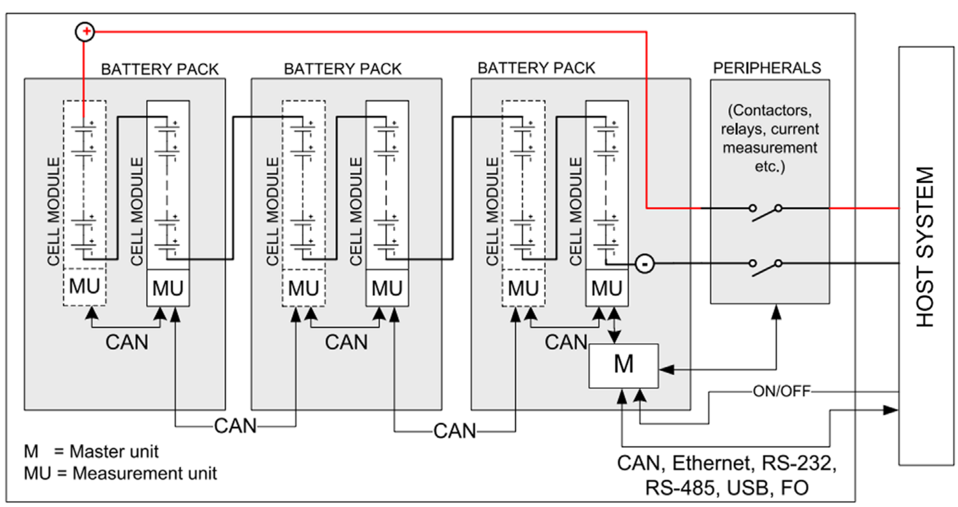

Fig. 8. Equalization energy system design of lithium ion battery pack management [40].

Table 1
Characteristics of different technologies.

Battery technologies	Life (cycle)	Energy density (Wh/L)	Self-discharge rate (%/month)	References
Traditional lithium ion battery	2000–2200	300–400	6–9	[18,20,39]
Graphene lithium ion battery	2400–2800	500–700	3–5	[12,22,35]
Lithium ion battery pack	1000–1200	400–500	9–11	[6,40,41]

4. Structure model and energy system design for lithium ion battery pack equalization

Battery management system for renewable energy vehicle needs improvement because multiple batteries are usually connected in series to get a higher voltage, but individual batteries cannot charge and discharge evenly [31–36], resulting in imbalance within battery pack and sharp deterioration of battery performance. The ultimate outcome is the failure of the entire pack at short lifetime with low reliability. Currently, the life expectancy of battery pack is significantly shorter than single battery. The average life of single battery ranges 5–7 years but battery pack is only 2–3 years, leading to low reliability and more accidents. Meanwhile, the load on power system varies frequently due to the dynamic road conditions, which further worsen the consistency between battery cells. Cells with lower capacity are

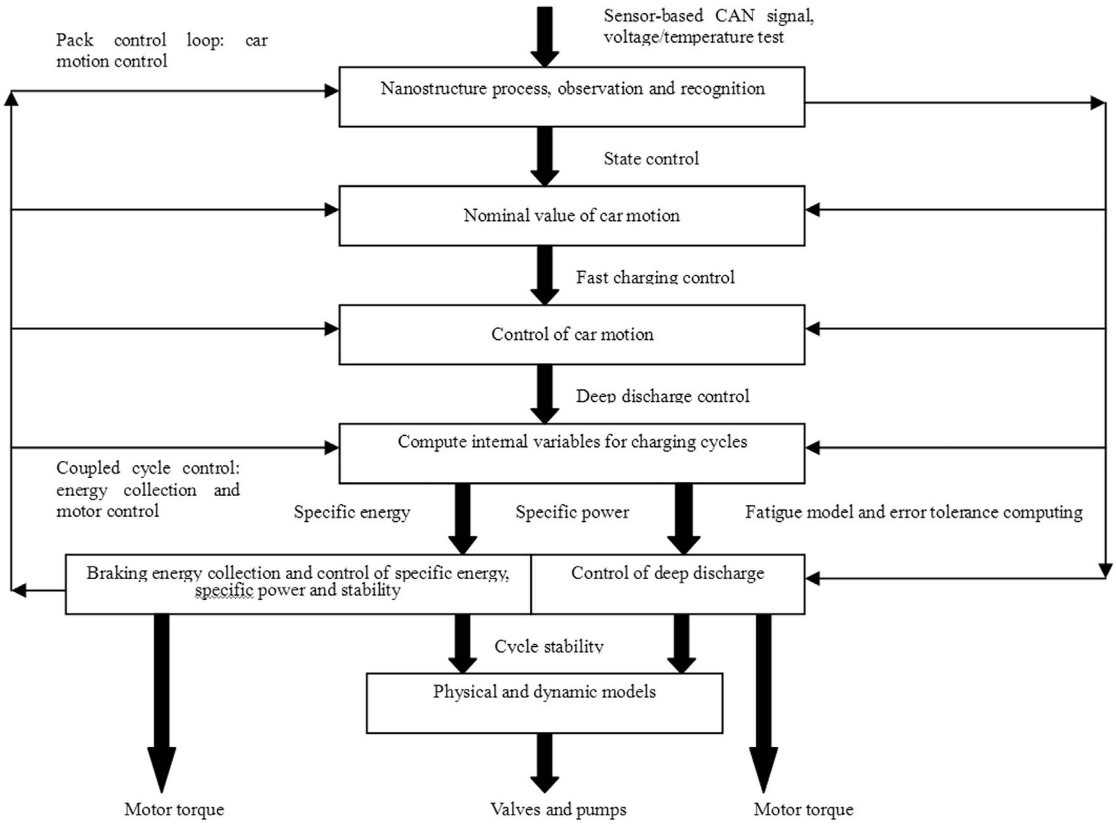

Fig. 9. Integrated control frameworks of structure model and energy system design for lithium ion battery of renewable energy vehicle.

prone to over-charge or over-discharge. Frequent over-charge/discharge accelerates battery aging and even causes deflagration [37–39]. As battery pack inevitably faces the difference between individual cells, measures must be taken to prevent cells from failing quickly. A balancing system is necessary for controlling over-charge/discharge in cells so as to keep the pack performance close to the level of single cells [40], as shown in Fig. 8.

A lithium-ion battery has no memory effect, implying that the capacity is not reduced if it is recharged without discharging fully in advance. However, the battery will be damaged if it is recharged when its capacity is full [18,20,39]. Compared with an ordinary lithium battery, a graphene lithium battery has more significant core values: higher volumetric specific energy, longer life, and a lower self-discharge rate. For the same output power, a lithium graphene battery's weight is only half that of a conventional lithium battery. Also, the size is 20% smaller [12,22,35]. The self-discharge rate of graphene lithium batteries is lower than 6% – an ordinary level of conventional lithium batteries. After being idle for one to two weeks, the battery can work normally [12,22,35]. The performance and safety of the battery mainly depends on the design of electrodes. Table 1 is a comparison of a traditional lithium battery, a graphene battery, and a battery pack according to different parameters. These parameters show that graphene batteries are outstanding in terms of energy density, life expectancy, and self-discharge rate. Being the core of renewable energy vehicles, a lithium battery also faces the issues of cell balancing and consistency, because a battery pack is composed of a large number of single cells arranged in serial, parallel, or hybrid forms. In theory, the life expectancy of a battery pack generally depends on the shortest life of a single cell. Only when individual batteries perform consistently and evenly can the pack's life approach that of a single cell. Typically, a single lithium battery can be used for more than 2000 times, but a battery pack can only be used for around 1000–1200 times [6,40,41]. With their rapid development in the past decade, powered lithium batteries have gained preponderance in the market of renewable energy vehicles. They have also become increasingly competitive for renewable energy applications.

5. Conclusion and prospects

Based on our research of structure models and energy systems [2,14,15,17,18,41] and micro-scale electromagnetic dynamics theories [42–45], we proposed an integrated control framework, as shown in Fig. 9, to regulate energy transfer between battery pack and cells to improve the energy conversion efficiency. Voltage and temperature measurement and balanced material are incorporated in the control system for cell collaboration and timely feedback [46–49]. For battery pack with large number of cells, the idea is to reduce the power losses in both cells and balancing circuits and estimate cell's state to identify AC impedance in real time [50–53]. A three-dimensional energy storage system is set up to strengthen the stability during cycles. Structure of electrode is further improved to allow deep discharge and better distribution of graphite and catalyst [54–57]. As high-capacity lithium ion battery is the direction of development for renewable energy vehicle, parallel structure made of small capacity cells shall be avoided. Because lithium-ion battery provides enough energy density and can work at high temperature, it serves as an ideal energy source to replace traditional internal combustion engines. Research on new material systems and structures enables lithium ion battery to better meet the requirements of renewable energy vehicle for deployment.

Acknowledgment

This work was supported by the National Natural Science Foundation of China (10972037) and the Science Fund of State Key Laboratory of Automotive Safety and Energy (KF11071).

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